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(54) Title: A METHOD OF PRODUCING A SILANIZED COMPOSITE FILLER AND A METHOD OF PRODUCING A COMPOSITE MATERIAL

(57) Abstract: The inventions includes a method of producing a silanized composite filler, said method comprises the steps of (i) providing a filler core material, and (ii) treating said filler core material, which is preferably an inorganic filler core material e.g. in the form of fibers or beads, with a silane coupling agent in the presence of a treatment medium comprising CO<sub>2</sub>. The best result is obtained when the silane coupling agent is relatively small, e.g. with molecular weight below 500g/mol. The invention also comprises a method of producing a composite material comprising the silanized composite filler, as well s the products obtained. The silanized composite filler is simple to produce and has a good adhesion to the polymer matrix of a composite material.

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A method of producing a silanized composite filler and a method of producing a composite material.

The invention relates to methods of producing a silanized composite filler  
5 and a composite material comprising said filler. The composite material produced according to the invention may in principle be used for any applications, but it is in particular useful when high strengths are desired.

BACKGROUND ART

10

Composites comprising fillers are common today. The interface between the filler and the polymeric material is of significant importance to the properties of the composite material. In particular the interface adjusts the mechanical resistance of the composite and the amount of filler which may be  
15 incorporated into a matrix.

In order to enhance the compatibility and the adhesion forces of fillers with the surrounding matrix, often thermoplastics or thermosets, it is commonly practiced to treat the surface of the filler. One of the most advanced and  
20 versatile method is the application of a coupling agent, such as phosphorus-based compounds, carboxylic acids, titanates, amines etc.

An often used coupling agent is functional silanes (as spray, aqueous or alcoholic solution, or as dry blend). Silanes ensure strong bonding between  
25 the filler and the silicium atom of the silane on the one hand, and improved bonding between the chemical groups of the silane and the surrounding matrix on the other hand. These silanes are available in differently reactive forms. As an example, chlorosilanes react fast with water-containing surfaces whilst alkoxysilanes can be employed if a lower reaction speed is  
30 preferred. Equally, a range of silane functionalities are available to afford compatibility with different plastic types. Some commercially available silanes or silane functionalities perform merely on the basis of chemical "likeness", others allow reactive cross-linking via e.g. vinyl bonds.

35 US 4,740,538 discloses coated minerals as fillers. The minerals are coated with an alkoxysilane using conventional coating methods e.g. by treatment in

a fluidized bed. US 5,332,429 discloses a method of treating fluoroaluminosilicate glass filler with a silanol in an aqueous solution optionally comprising alcohol or ketone solvents.

## 5 SUMMARY OF INVENTION

The objective of the present invention is to provide an alternative or even improved method of applying a coupling agent to a filler for a composite material, which method is simple to use and inexpensive, and whereby a  
10 good or even improved bonding between filler and composite matrix material can be obtained.

This and other objectives as disclosed in the following description have been achieved by the invention as it is defined in the claims and described in the  
15 description.

The inventor has thus found that by using CO<sub>2</sub> as solvent, silane coupling agents can be applied to the surface of a filler in a simple and effective process. Depending on the steps of the coating process, the total  
20 composition of the solvent, pre and after treatments and the selection of silane coupling agents, a number of improvements, separately or in combinations, may be obtained as it is further described in the following.

Thus, the method of the invention contributes to the art by providing new  
25 alternatives for use giving the user the desired benefits.

Furthermore the inventor has identified new uses of the silanized filler, which are highly beneficial as it will be disclosed in the following.

## 30 DISCLOSURE OF INVENTION

The method of the invention for producing a silanized composite filler comprises the steps of

35 i) providing a filler core material, and

ii) treating said filler core material with a silane coupling agent in the presence of a treatment medium comprising CO<sub>2</sub>.

The filler core material may in principle be of any type of material or combinations of materials which under the treatment conditions are in solid form. Such filler core materials are generally known in the art, and examples hereof are e.g. disclosed in US 2003/0083516, US 5,968,652, US 2001/00366617, US 5,861,445 and US 4,740,538.

10 The filler core material may e.g. be selected for adding properties such as mechanical properties e.g. strength, wearing, durability, low-weight, etc. to the final matrix into which is to be incorporated. The core material may also be selected in order to reduce cost, to change surface characteristics or for other reasons.

15 In one embodiment, the filler core material is selected from the group of metals such as, aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc; metal oxides/ hydroxides such as alumina trihydrate, oxides of aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, antimony and zinc; metal salts, such as phosphates, sulfides, and sulfates; minerals such as spodumene, mica, montmorillonite, kaolinite, bentonite, hectorite, beidellite, attapulgite, chrysolite, garnet, saponite, and hercynite; 20 ceramic materials such as hydrated or anhydrous silicas, silica, silicate glass, quartz, calcium silicates, calcium-magnesium silicates, barium silicates, sodium-alumino-silicates, calcium-alumino-silicates, calcium-sodium-alumino silicates; clays (aluminum silicates) such as halloysite, montmorillonites including sodium and magnesium bentonites; synthetic or natural zeolites; and synthetic or natural talcs (magnesium silicates); and 25 organic materials such as carbon black; graphite, granulated or milled thermoplastics or thermosets such as recycled or virgin polymer resin or rubber; wood-derived materials such as lignin, lignosulfates, Kraft lignin, cellulose and mixtures thereof.

35

In one embodiment, the filler core material is selected from the group of silica, fumed silica, silica made by sol-gel chemistry, silicate glass, quartz, barium silicate, barium sulphate, barium molybdate, barium methacrylate, barium yttrium alkoxy, strontium silicate, barium borosilicate, strontium borosilicate, borosilicate, lithium silicate, amorphous silica, calcium phosphate, calcium carbonate, alumina, aluminium zirconia, tin oxide, tantalum oxide, niobium oxide, and titania glass, carbon black, graphite, cristobalite, silica, zircon-silica, calcium metasilicate (e.g. wollastonite), calcium magnesium silicate, and mixtures thereof.

10 The filler core material may in one embodiment be porous, such as with pores e.g. as described for the filler disclosed in US 5,968,652.

In one embodiment, the filler is nonporous particles.

15 The filler may in principle have any shape and size e.g. in the form of particles or fibers or mixtures thereof.

20 The type, the size and the shape of the desired filler depend largely on their intended use e.g. in paints, in dental cements, in insulating materials and e.t.c.

In one embodiment, the filler core material comprises or preferably is in the form of particles having particle diameters in the range from about 0.001  $\mu\text{m}$  (1 nm) to about 4 mm, such as for dental cement use 0.001-100  $\mu\text{m}$  (e.g. between 0.005 and 1.0  $\mu\text{m}$ ), such as 1 mm to 4 mm for use in road marking materials. By the term "having particle diameters" is meant - unless other is specified - that at least 95 % by weight, preferably at least 98 % by weight of the particles are within the specified range as measured using sieving.

30 In one embodiment, the particles and/or fibers have a BET surface area of between 0.1 and 1000  $\text{m}^2/\text{g}$ , such as between 1 and 500  $\text{m}^2/\text{g}$  measured using gaseous nitrogen.

35 In one embodiment, the filler core material comprises or preferably is in the form of fibers. A fiber means in this context a unit with a length to diameter

aspect ratio of 2 or more. The fibers may be chopped or non- chopped, single crystalline or polycrystalline, single filaments or polyfilaments. The fibers may e.g. have an aspect (length to diameter) ratio of 2 to 1000, such as from 2 to 300, such as from 3 to 200, such as preferably at least 20. The diameter of the fibers may preferably being in the range of up to about 3000  $\mu\text{m}$ , such as in the range from 0.001  $\mu\text{m}$  to 100  $\mu\text{m}$ , such as in the range from 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ . In particular glass fibers are preferred due to their low cost and high strength. Such glass fibers may advantageously be used in a polymer glass fiber matrix as further disclosed below.

10

In one embodiment, the filler core material is spherical hollow glasses (bobbles) e.g. with a particle size between 0.01 and 100  $\mu\text{m}$ . This hollow filler core material may preferably be used in insulating materials e.g. mixed in a ratio of 10-70 % by weight.

15

In the method according to the invention it has been found that the covering of filler core material when the filler core material is relatively small, such as with a major amount (50 % by weight measured using sieving) of filler with diameter or particle size less than 10  $\mu\text{m}$ , or even less than 1  $\mu\text{m}$ , may be improved as compared with using prior art methods due to the fact that the low surface tension of pressurized  $\text{CO}_2$  allows diffusion and prevents baking together of the filler core material particles/fibers. Such baking together of filler core material particles/fibers is often seen in prior art methods. This effect may be further improved by using a surfactant as described further below.

25

In one embodiment, the filler core material comprises or is in the form of a woven or non-woven fiber unit, such as a fiber mat.

30 The term "silane coupling agent" includes silane components as well as silanol compositions e.g. with 1-3 OH-groups. Silanol is hydrolyzed silane (e.g. alkoxy silans and chloro silans).

In the following the invention is described with silane but it should be understood that the corresponding hydrolyzed silanes may be used as well.

35

In one embodiment, the silane coupling agent is in the form of a monomeric, oligomeric or polymeric alkoxy- or chlorosilane coupling agent such as ethylenically-unsaturated alkoxy- or chlorosilane coupling agent or a combination or mixture thereof. In general, it is desired that the silane coupling agent comprises at least one of the groups vinyl groups, allyl groups, alkyl groups, styryl groups, aromatic groups, chloromethylaromatic groups, amino groups, isocyanate groups, halogen atoms such as fluorine or chlorine or bromine atoms, epoxide groups, mercapto groups, acrylic groups, metacrylic groups, silazane groups, and azido groups.

10

The method of the invention is highly beneficial when the silane coupling agent includes alkoxy- or chlorosilanes in that alkoxy- or chlorosilanes yield alcohols which in prior art methods are difficult to remove upon deposition onto surfaces containing hydroxyl groups, and chlorosilanes yield HCl which is equally difficult to remove and poses HSE risks for operating personnel. In medical applications, HCl needs to be removed quantitatively. These by-products as well as HCl are easily removed using CO<sub>2</sub> containing medium. Also water and alcohol as carriers, as well as silanols formed in the reaction of chlorosilane with water or alcohol, which need to be removed as they adversely effect the composite stability, can easily be removed using CO<sub>2</sub> containing medium according to the invention.

15

In one embodiment, it is desired that the silane coupling agent is selected so that it is capable of bonding chemically via ionic and/or covalent bondings to the filler core material. In another embodiment, the silane coupling agent is selected so that it is capable of bonding physically to the filler core material e.g. by adhesion, hydrogen bondings or by cross-linking to itself. In one embodiment, both chemical and physical bondings will be provided between the silane coupling agent and the filler core material.

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In one embodiment, it is desired that the silane coupling agent is selected so that it is capable of bonding chemically via ionic and/or covalent bondings to the polymer matrix material. In another embodiment, the silane coupling agent is selected so that it is capable of bonding physically to the polymer matrix material e.g. by adhesion, hydrogen bondings or by cross-linking to

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itself. In one embodiment, both chemical and physical bondings will be provided between the silane coupling agent and the polymer matrix material.

In one embodiment, the silane coupling agent is selected from the group consisting of the following silanes or the corresponding silanols:  
5 vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri-(2-methoxyethoxy)-silane, vinylbenzylcationic silane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane,  
10  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane, isocyanatoethyltrimethoxysilane, isocyanatopropyltrimethoxysilane, isocyanatopropyltriethoxysilane, N-(3-trimethoxysilylpropyl)-N-methyl-N,N-diallyl ammonium chloride, trimethoxysilylpropylisothiuronium chloride, N-trimethoxysilylpropyltributylammonium bromide, N-trimethoxysilylpropyl-  
15 N,N,N-trimethylammonium chloride,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -chloropropyltrimethoxysilane; n-alkylsilanes, n-alkyldichlorosilanes, n-alkyltrichlorosilanes, such as n-hexyltrichlorosilane, n-octyltrichlorosilane, n-decyltrichlorosilane, n-dodecyltrichlorosilane, and mixtures thereof.

20

In the present invention it is possible to use silane coupling agent carrying relative large substituents, which is difficult or impossible to dissolve in water and organic solvents, and thereby not applicable in practice in the prior art methods, because the treatment proceeds from an emulsion with long  
25 reaction times and side reactions competing with the surface treatment as consequence. This is due to the fact that CO<sub>2</sub> has shown to exhibit excellent solubility properties for silane coupling agent under pressure. Furthermore, short reaction times are achieved in general using the CO<sub>2</sub> containing medium according to the invention.

30

In one embodiment, the silane coupling agent has a relatively low molecular weight, such as preferably below 500 g/mol, e.g. between 150 and 400 g/mol. By using such low molecular silane coupling agent the inventor has found that a particularly improved silanized composite filler can be obtained.  
35 It has thus been found that by using such low molecular silane coupling agent the coating onto the filler core material has shown to become highly



homogenous, and with increased bonding strength, which furthermore results in a silanized composite filler which can be bonded with a very high bonding strength to a composite matrix.

- 5 In one embodiment, the silane coupling agent has a surface tension which is less than the surface tension of water (72 dyn/cm at 20 degree C).

In the method according to the invention the treatment medium comprises CO<sub>2</sub>. The amount of CO<sub>2</sub> should preferably be a significant amount, and even  
10 more preferred a dominant amount such as at least 50 % by weight, such as at least 75 % by weight, such as at least 85 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as essentially pure CO<sub>2</sub>.

The remaining part of the treatment medium may in principle be anything  
15 that does not prevent the desired reaction between the filler core material and the silane coupling agent.

In one embodiment, the treatment medium comprises up to 50 % by weight of water, such as up to 25 % by weight of water, such as up to 10 % by  
20 weight of water, such as up to 5 % by weight of water, such as up to 1 % by weight of water.

Not all silanes e.g. silanetriols with hydrophobic residues are entirely soluble in the treatment medium as well as in water. The limit of the solubility in  
25 water is given by 6 carbons in an aliphatic and 7 carbons in an aromatic silane. Longer residues lead to the formation of micelles with a hydrophobic core. The tendency of phase separation increases again when the silanetriol starts to polycondense, because the resulting oligosilanes are more or less insoluble in water. The stability of the silanetriol solutions depends strongly  
30 on their pH. A pH-range of 2-4 is most favorable for a maximum stability. (H. R. Kricheldorf, Silicon in Polymer Synthesis, Springer Verlag Berlin, 1996, p.418-421).

In sc-CO<sub>2</sub> (or liquid CO<sub>2</sub>), silanetriols with longer carbon chains are soluble.  
35 Moreover the pH in sc-CO<sub>2</sub> is between 2.8 and 3.0 in a temperature range of

25 to 70°C and a pressure of 70 to 200 atm. in the presence of small amounts of water.

It is in general preferred that the silane coupling agent is soluble in the treatment medium. For this reasons silane coupling agent having low  
5 molecular weight e.g. between 150 and 500 g/mol is preferred.

For other situations it is sufficient that the silane coupling agent can be dispersed in the treatment medium.

10

In one embodiment, the treatment medium comprises up to 50 % by weight of an organic solvent such as alcohols, ketones, paraffins, ethers, amines, aromatics, such as up to 25 % by weight of organic solvent, such as up to 10 % by weight of organic solvent, such as up to 5 % by of organic solvent.

15

In prior art methods the amount of water and organic solvents used is generally relatively high, and in most prior art methods more than 90 % by weight of the solvent used for silanising is composed of water and organic solvent.

20

By the method of the present invention it has thus in one embodiment been possible to reduce the amount of water and organic solvent used to a total of less than 50 % by weight, which results in reduced risk of elimination, less need for drying or removing solvents, and furthermore reduced need for  
25 working with organic solvents, and thereby also a reduced pollution risk.

Furthermore, it has been found that in this embodiment using none or only low amounts (less than 50 % by weight, or even less than 20 % by weight) of water and organic solvents, the coupling agent is more effective in forming  
30 chemical bondings with the filler core material.

In one embodiment, it is desired that the treatment medium comprises a surfactant, e.g. up to about 3 %, such as up to about 1 %, such as up to about 0.2 % by weight of surfactants.

35

The surfactants may in principle be any type of surfactant such as anionic, cationic, non-ionic and amphoteric surfactants. It has surprisingly been found that the detergent results in a faster process, which also may provide a larger concentration of silane coupling agents bonded onto the surface of the  
5 filler core material. It is believed that the major purpose of the detergent is to modify the surface tension of the filler core material to increase wetting properties with the treatment medium.

Thus, by using a surface tension lowering surfactant the wettability of the  
10 filler core and the silane coupling agent with the CO<sub>2</sub> treatment medium may be increased and thereby improving the reaction speed.

The detergent may preferably be in form of a liquid or in the form of a  
15 solution.

In one embodiment, the detergent should preferably be added to keep the surface tension below a desired level, e.g. 50 dyn/cm, more preferred in the range between 20 and 45 dyn/cm.

20 In one embodiment, the CO<sub>2</sub> is in its liquid state during the treatment step. At least part of the silane coupling agent should preferably be dissolved or dispersed in the treatment medium. Thus, in one embodiment the silane coupling agent is partly or preferably totally dissolved or dispersed in the treatment medium containing CO<sub>2</sub>.

25 In one embodiment, the CO<sub>2</sub> is in its supercritical state during the treatment step. At least part of the silane coupling agent should preferably be dissolved or dispersed in the treatment medium. Thus, in one embodiment the silane coupling agent is partly or preferably totally dissolved or dispersed in the  
30 treatment medium containing CO<sub>2</sub>.

During the treatment step the CO<sub>2</sub> may convert from one state to another. In one embodiment, the CO<sub>2</sub> is changing from its liquid state/gas state to its supercritical state during the treatment step. This may be performed by  
35 changing the pressure and/or the temperature. By providing a change of the CO<sub>2</sub> state from its liquid state/gas state to its supercritical state during the

treatment step, the treatment may be speeded up. Furthermore this change of state may result in an instant intermixing of the filler core/silane coupling agent and the treatment medium, whereby additional stirring may be superfluous, thereby resulting in a saving in equipment.

5

The amount of silane coupling agent to CO<sub>2</sub> containing medium may vary depending on the filler core material and the silane coupling agent used. In one embodiment, the amount of silane coupling agent to treatment medium is between 0.001:1 w/w and 1:1, preferably in the range of 0.01:1 w/w and  
10 0.1:1.

In certain applications the inventor of the present invention has found that particles with relatively small amounts of silane coupling agent when incorporated in a polymeric matrix result in surprisingly good cohesion  
15 properties. In one embodiment, it is therefore desired that the amount of silane coupling agent is selected so that the final filler comprises between 0.01 % and 1 %, such as between 0.05 % and 0.5 %, such as between 0.08 % and 0.2 % by weight of the silane coupling agent.

20 In one embodiment, where the amount of silane coupling agent is selected so that the final filler comprises between 0.01 % and 1 %, such as between 0.05 % and 0.5 %, such as between 0.08 % and 0.2 % by weight of the silane coupling agent, it is furthermore desired that the filler core material has a particle size so that the BET surface area measured using N<sub>2</sub> gas is 50 m<sup>2</sup>/g or higher, such as between 100 and 100 m<sup>2</sup>/g. Such a silanized filler is particularly useful in a dental cement as described further below.

In one embodiment, where the amount of silane coupling agent is selected so that the final filler comprises between 0.01 % and 1 %, such as between  
30 0.05 % and 0.5 %, such as between 0.08 % and 0.2 % by weight of the silane coupling agent, it is furthermore desired that the filler core material is in the form of glass fibers having a length to diameter aspect ratio of 20 or more, such as from 25 to 500, such as from 50 to 200.

The pH value of the treatment medium may advantageously be adjusted to either 5 or less or 8 or higher to thereby promote hydrolysis of the silane. The added surfactant may e.g. additionally be used for adjusting pH value.

- 5 In one embodiment of the invention, the filler core material is subjected to a cleaning step prior to or simultaneously with the silane treatment step. This cleaning step may preferably comprise the step of subjecting the filler core material to a cleaning medium comprising CO<sub>2</sub>.
- 10 The cleaning medium may have a composition as disclosed above for the treatment medium. The cleaning medium and the treatment medium may be different from each other or they may be equal. In one embodiment, the cleaning medium and the treatment medium have essentially equal composition. This embodiment is particularly simple to perform as the
- 15 cleaning and treatment may be carried out simultaneously or immediately after each other in the same reactor, using the same medium as cleaning medium and treatment medium. In order to obtain a high cleaning effect it is preferred that the cleaning step is initiated prior to initiation of the treatment step, such as preferably at least one minute prior to initiation of the treatment
- 20 step, such as preferably at least 5 minutes prior to initiation of the treatment step, such as preferably at least 10 minutes prior to initiation of the treatment step, such as preferably at least 15 minutes prior to initiation of the treatment step. The treatment step may e.g. be initiated simply by adding the silane coupling agent to the reaction chamber.
- 25 The combined cleaning-treatment method is highly beneficial first of all because of its simplicity, but also because of the improved filler material obtained. The simplicity of the combined cleaning-treatment method is due to the fact that the method may be carried out virtually as a one step method.
- 30 The filler core material and the cleaning medium are placed in a reactor and the pressure and e.g. temperature are regulated to the desired level, after a certain time, which optimally is at least 5 minutes, the silane coupling agent is added to the reaction chamber optionally together with additional CO<sub>2</sub> or other additional parts of the treatment medium. Simultaneously the
- 35 temperature and/or pressure may be adjusted to the treatment conditions, and the treatment is performed.

After the treatment, the silane treated filler core material may additionally be subjected to an impregnating step comprising depositing additional components to the silane treated filler core material. Such an impregnation step is well known in the art, and an example hereof is disclosed as the impact modifiers in US 4,740,538.

In one embodiment, the impregnating step comprises depositing one or more impregnating components in the form of organic components, such as polymer or polymer precursors (including monomers, dimers and oligomers) to the silane treated filler core material, said impregnating components preferably being added from an impregnating medium comprising CO<sub>2</sub>.

In one embodiment, the impregnating component(s) is/are selected from the group consisting of mono or multifunctional monomers, such as monomers comprising one, two or more ethylenically unsaturated double bonds e.g. including unsaturated amides such as 2-acrylamidoglycolic acid, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, tetra acrylamido glycuril ("TAGU") and diethylenetriamine tris-acrylamide; linear, branched or cyclic polymer of ethylenically unsaturated monomers, polyester, polyamide, polyether, polyethyleneglycol, polysaccharide, cellulose, polypropylene, polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde; and mixtures thereof.

In one embodiment, the impregnating component(s) is/are selected from the group consisting of mono-, di- or polyfunctional acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, styryl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate ("TEGDMA"), tetraethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate (e.g., "PEG200 DMA", "PEG400 DMA" and "PEG600 DMA" with an average of 4.5, 9 and 13.6 ethyleneglycol groups or "units" respectively), 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,3-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate,

sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, tris-hydroxyethylisocyanurate triacrylate, beta-methacrylaminoethyl methacrylate, 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl]-propane ("BIS-GMA"), 2,2-bis[4-(2-methacryloyloxyethoxy)-phenyl]propane, 2,2-bis[4-methacryloyloxyphenyl]propane, "SARTOMER" 350 ("SR350", Sartomer Corp.) and mixtures thereof.

The impregnating medium may have a composition as disclosed above for the treatment medium. The impregnating medium and the treatment medium may be different from each other or they may be equal. In one embodiment, the impregnating medium and the treatment medium have essentially equal composition. This embodiment is particularly simple to perform as the cleaning and treatment may be carried out immediately after each other in the same reactor, using the same medium as impregnating medium and treatment medium.

The silane treated filler core material may additionally be subjected to a curing step for further curing of the silane coating and optional impregnation of the coating. The curing step may e.g. include subjecting the silane treated filler core material to increased temperature or radiation or other activating treatments as are generally known in the art.

Curing may preferably be performed in the treatment reactor under inert gas atmosphere. Thereby oxidation and degradation risks are minimized.

The silane treated filler core material may further be subjected to a final rinsing step for removing soluble products, said rinsing step preferably including subjecting the silane treated filler core material to a flushing with a flushing medium comprising CO<sub>2</sub>, such as at least 50 % by weight, such as up to about 75 % by weight, such as up to about 85 % by weight, such as up to about 90 % by weight, such as up to about 95 % by weight of CO<sub>2</sub>, such as essentially pure CO<sub>2</sub>, the remaining of the flushing medium preferably consisting of water, organic solvents and/or surfactants.

The flushing medium may have a composition as disclosed above for the treatment medium. The flushing medium and the treatment medium may be different from each other or they may be equal. In one embodiment, the flushing medium and the treatment medium have essentially equal  
5 composition. This embodiment is particularly simple to perform as the cleaning and treatment may be carried out immediately after each other in the same reactor, using the same medium as impregnating medium and treatment medium.

10 The treatment medium (or medium if the same is used for all steps) may be recirculated, and extracted components such as reaction by-products (e.g. HCL) may be removed and thereby pollution and HSE risk may be reduced.

In one embodiment, the cleaning medium, the treatment medium, the  
15 impregnating medium and the flushing medium have essentially the same composition, which provides a very simple method.

The final silane treated filler core material may, if necessary, be subjected to a drying step. In most situations this step is not necessary as the final silane  
20 treated filler is already dry due to the use of the medium(s).

In one embodiment, the "solvent" carbon dioxide is completely removed upon depressurizing. Dynamic drying is therefore not needed.

25 The invention also relates to a method of producing a composite material comprising the steps of producing a silanized composite filler using the method as described above and mixing said silanized composite filler with an optionally curable composite matrix material. Thereby it is possible to provide  
30 either a composite material with increased filler-matrix adhesion due to increased chemical compatibility, or to provide a precursor composite material and curing said precursor composite material, preferably using temperature or radiation.

The composite matrix material may in principle be any type of polymeric  
35 material.



The composite matrix material may in one embodiment be selected from the group consisting of -linear, branched or cyclic polymer of monomers such as ethylenically unsaturated monomers or difunctional materials such as diols, diamines, diisocyanates, dicarboxylic acids, the thus derived polymers being  
 5 selected from the group of polyester, polyamide, polyether, polyethyleneglycol, polysaccharide, cellulose, polyethylene, polypropylene, polybutylene, polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), polystyrene, polysulfone, polycarbonate, fluoropolymers such as polytetrafluoroethylene, polyvinylidene fluoride, synthetic and natural rubber,  
 10 thermoplastic elastomer, silicone rubber, phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde, and mixtures thereof.

The composite matrix material may in one embodiment be selected from the group consisting of mono-, di- or polyfunctional acrylates and methacrylates  
 15 such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, styryl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate ("TEGDMA"), tetraethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate (e.g., "PEG200 DMA",  
 20 "PEG400 DMA" and "PEG600 DMA" with an average of 4.5, 9 and 13.6 ethyleneglycol groups or "units" respectively), 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,3-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate,  
 25 sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, tris-hydroxyethylisocyanurate triacrylate, beta-methacrylaminoethyl methacrylate, 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl]-propane ("BIS-GMA"), 2,2-bis[4-(2-methacryloyloxyethoxy)-phenyl]propane,  
 30 2,2-bis[4-methacryloyloxyphenyl]propane, "SARTOMER" 350 ("SR350", Sartomer Corp.) and mixtures thereof.

In one embodiment, the curing between the silanized filler and the composite matrix is afforded by cross linking saturated or unsaturated organic groups  
 35 attached to both the filler and present in the composite matrix, said cross linking e.g. being provided by applying radiation such as UV-light or gamma-

radiation and/or by activation (decomposition) of previously admixed peroxides or azocompounds such as dicumylperoxide or bis-[t-butylperoxy] compounds or azo-bis-isobutyronitril.

The composite material may in principle be for any type of use. In one embodiment, the composite material is a composite material for use in the industrial, automotive, aviation and aerospace sector, such as parts which can be produced by injection moulding, extrusion, calendaring or moulding.

In one embodiment, the composite material is a dental cement.

In one embodiment of the dental cement, the filler core material is selected from the group consisting of crystalline quartz, pyrolytic silica ( $\text{SiO}_2$ ), lithium aluminium silicate, glass, boron glass and barium glass. All of these filler materials have high hardness, chemical inertness and refractive index and opacity close to that of tooth structure.

In one embodiment for a dental cement, it is particularly preferred that the filler core material is a glass bead, preferably in the form of relatively fine powder, such as a glass bead with a particle size so that the BET surface area measured using  $\text{N}_2$  gas is  $50 \text{ m}^2/\text{g}$  or higher, such as between 100 and  $200 \text{ m}^2/\text{g}$ .

In one embodiment of the dental cement, the filler core material is an inorganic material and has a particle size between  $0.005$  and  $1.0 \mu\text{m}$ .

The filler core material for the dental cement may preferably be treated so that the amount of silane coupling agent is selected to provide the glass bead with between  $0.01 \%$  and  $1 \%$ , such as between  $0.05 \%$  and  $0.5 \%$ , such as between  $0.08 \%$  and  $0.2 \%$  by weight of the silane coupling agent.

The dental cement should preferably be relatively highly filled with the silanized composite filler (preferably silanized glass beads), such as with a filling degree of at least  $10 \%$  by weight, such as between  $15$  and  $90 \%$ , such as between  $50$  and  $80 \%$  by weight of silanized composite filler of the total dental cement.

The polymer matrix could in principle be any type of polymer matrixes, but preferably the matrixes which are particularly adapted for dental use include Bisphenol-diglycidol methacrylate (Bis-GMA), Urethane dimethacrylate (UDMA), Triethylenglycol dimethacrylate (TEGDMA) and Bisphenol A  
5 polyethylene glycol diether dimethacrylate (Bis-EMA). The skilled person will easily be able to identify useful polymer matrixes for the dental cement.

In one embodiment, the polymer matrix is light curable, and includes a catalyst which is already mixed into the paste, but does not become active  
10 until illuminated with a strong light.

The dental cements may e.g. further comprise one or more of the following components zinc oxide-eugenol, zinc phosphate, zinc silico-phosphate, zinc-polyacrylate, zinc-polycarboxylate, glass ionomer, colour modifiers and  
15 pigments (e.g. titan dioxide and metal oxide pigments).

The invention also relates to the use of composite material as a dental cement, as well as the dental material itself.

20 The dental cement according to the invention has been found to have a very high biocompatibility, and does not result in release of excessive amounts of fluoride which is a common problem of prior art dental cements. Furthermore the dental cement of the invention has a high cohesiveness, comparable or even improved with respect to prior art dental compositions. Finally the dental  
25 cement according to the invention can be produced at lower cost than comparable conventional dental cements.

In one embodiment, the composite material is a paint.

30 For a paint it is particularly preferred that the filler core material is mineral fibers or beads e.g. glass beads, preferably in the form of relatively fine powder, such as glass beads with a particle size so that the BET surface area measured using  $N_2$  gas is  $50 \text{ m}^2/\text{g}$  or higher, such as between 100 and  $100 \text{ m}^2/\text{g}$ . In one embodiment, the glass beads for the paint have a particle  
35 size between  $0.5 - 100 \text{ }\mu\text{m}$ . The glass beads may preferably be of mineral glass.

In one embodiment of the paint, the filler core material is fibers, such as mineral fibers e.g. glass fibers. The fibers may preferably have a diameter of from 0.5 to 3000  $\mu\text{m}$ . The aspect ratio may e.g. be as disclosed above.

5 The mineral fibers or beads may preferably be treated so that the amount of silane coupling agent is selected to provide the mineral fibers or beads for the paint with between 0.01 % and 2 %, such as between 0.1 % and 1 %, such as about 0.5 % by weight of the silane coupling agent.

10 The filling degree in the paint may vary largely in dependence of the use of the paint, but normally it will be up to about 30 % by weight, such as between 10 and 25 % by weight of the paint in its dilution as recommended for use.

The polymer matrix could in principle be any type of polymer matrixes, but  
15 preferably the matrixes which are particularly adapted for paints such as epoxy paint.

The paint may e.g. further comprise pigments, thinner, dryer and other additives as are normally used in conventional paints

20 The invention also relates to the use of composite material as a paint cement as well as the paint itself.

The paint according to the invention has been found to have a desirably high  
25 cohesiveness and further it has been found that the silanized glass beads result in a corrosion protection which makes the paint highly useful in e.g. ship paint applications.

In one embodiment, the composite material is a polymer glass fiber matrix

30 The glass fibers may in this polymer glass fiber matrix preferably have a relatively high length to diameter aspect ratio, such as preferably at least 20 or more, such as from 25 to 500, such as from 50 to 200.

The polymer matrix may e.g. be a thermoplast or a non-thermoplast (curable polymer). In principle the polymer matrix may be as disclosed in the general method of the invention above, e.g. PE, PP, PA, epoxy, PET and etc.

5 In one embodiment of the polymer glass fiber matrix, the silane coupling agent is selected so that the final glass fiber filler comprise between 0.01 % and 1 %, such as between 0.05 % and 0.5 %, such as between 0.08 % and 0.2 % by weight of the silane coupling agent. This polymer glass fiber matrix is particularly useful as material for applications in the automobile and ship  
10 industry.

In one embodiment of a polymer glass fiber matrix for use in the automobile and ship industry, the glass fibers (e.g. PPG (3310), E-glass, 3-6 mm in length) are silanized using octyltriethoxysilan as silane coupling agent and  
15 thereafter the silanized glass fibers are mixed with PE. The amount of silane may e.g. be 1 wt% silane or 0.2 wt% silane or anything there between.

In one embodiment of a polymer glass fiber matrix for use in the automobile and ship industry, the glass fiber mat is silanized using 3-(triethoxysilyl)-propylamin as silane coupling agent and thereafter the silanized glass fibers  
20 are mixed with PET.

The invention also relates to the use of the polymer glass fiber matrix in the automobile and ship industry as well as the polymer glass fiber matrix itself.

25 One embodiment of a polymer glass fiber matrix according to the invention is for use in the pump industry, in particular for cooling wheels for pumps. In one embodiment the glass fibers are silanized using 3-(triethoxysilyl)-propylamin as silane coupling agent and thereafter the silanized glass fibers  
30 are mixed with nylon (PA). The amount of silane may e.g. be 1 wt% silane or 0.2 wt% silane or anything there between.

## Examples

### Example 1

- 5 Large rolls of fibers or large-scale composite fillers are placed directly into a pressure reactor. Small-scale fillers, such as below 1 mm in size, are placed into gas-permeable bags for treatment.

The treatment steps include at least one of the following processes:

10

- cleaning using  $\text{CO}_2$  containing cleaning medium and optionally surfactant,
- silane treatment as described above,
- impregnation with other materials which can be deposited from carbon dioxide containing medium, such as resins such as bis-GMA (Bisphenol A diglycidyl ether dimethacrylate), TEGDMA (triethylene glycol dimethacrylate), UDMA (urethane dimethacrylate), bis-EMA (Bisphenol A polyethylene glycol diether dimethacrylate), and others particularly useful in the area of dental composites, or materials such as precursors of polymers such as styrene, isocyanates, glycols, acrylates and the like, for the purpose of improved binding to composite compositions,
- curing, i.e. treatment at elevated temperature for a period of time,
- final rinsing, i.e. flushing with pure carbon dioxide, to remove soluble products.

25

A specific embodiment relates to a new material designed for windmill wings. Traditionally, silane-treated glass fiber mats and epoxy resins are employed. According to this invention, glass fiber mats are treated in pressurized gas, especially containing carbon dioxide, and with silanes carrying long alkyl chains, vinyl-, aromatic- and other groups. The glass fibers are thereafter moulded together with polyolefins, polyesters, polyurethanes, silicones and similar thermoplastics. This results in wings with comparable mechanical properties, but with the advantages of (i) lower production and material costs, (ii) recycleability.

35

## Example 2

Glass filler core material (fibers or beads), and silane coupling agent are placed separately in a pressure reactor. They may be positioned in different  
5 compartments of the reactor, or the silane coupling agent may be dosed into the reactor at a later stage after pressurizing, and the glass material may optionally be held in gas and liquid permeable bags to ease handling. Carbon dioxide is added to the reactor typically up to a pressure of 40 bars and a temperature of 15 degree C. Higher and lower temperatures and  
10 pressures may be applied.

The reactor content is agitated, either by rotating the reactor itself (for small  
scale experiments) or by rotating or moving baskets within the reactor, or by  
moving and pumping around the dense phase medium (CO<sub>2</sub>). After 15-30  
15 min, reaction is completed, and products are either post-cured 24 hrs at room temperature, alternatively 2-4 hours at around 100 degree C.

Stainless steel reactors are used in our experiments, and silane reaction with  
stainless steel is found to be negligible.

20

For handling different silane types, the following rules of thumb are applicable:

1. Long-chain silanes are preferably handled at high pressure because their solubility increases with pressure.
- 25 2. Good dispersion and dilution of silanes is recommendable due to the high reaction speed. Dilution helps to maintain a silane concentration sufficiently high so as to enable surface reaction on all glass surfaces brought into the reactor.
3. For very reactive silanes, it is recommendable to dose the silane  
30 successively into the reactor and / or to agitate glass fibers or glass beads simultaneously.

### Claims

1. A method of producing a silanized composite filler, said method comprises the steps of
  - 5 i) providing a filler core material, and
  - ii) treating said filler core material with a silane coupling agent in the presence of a treatment medium comprising CO<sub>2</sub>.
2. A method according to claim 1, wherein said filler core material is  
10 selected from the group of metals such as, aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc; metal oxides/ hydroxides such as alumina trihydrate, oxides of aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium,  
15 manganese, iron, cobalt, nickel, copper, antimony and zinc; metal salts, such as phosphates, sulfides, and sulfates; minerals such as spodumene, mica, montmorillonite, kaolinite, bentonite, hectorite, beidellite, attapulgite, chrysolite, garnet, saponite, and hercynite; ceramic materials such as hydrated or anhydrous silicas, silica, silicate glass, quartz, calcium silicates,  
20 calcium-magnesium silicates, barium silicates, sodium-alumino-silicates, calcium-alumino-silicates, calcium-sodium-alumino silicates; clays (aluminum silicates) such as halloysite, montmorillonites including sodium and magnesium bentonites; synthetic or natural zeolites; and synthetic or natural talcs (magnesium silicates); and organic materials such as carbon black;  
25 graphite, granulated or milled thermoplastics or thermosets such as recycled or virgin polymer resin or rubber; wood-derived materials such as lignin, lignosulfates, Kraft lignin, cellulose and mixtures thereof.
3. A method according to claim 2, wherein said filler core material is  
30 selected from the group of silica, fumed silica, silica made by sol-gel chemistry, silicate glass, quartz, barium silicate, barium sulphate, barium molybdate, barium methacrylate, barium yttrium alkoxo, strontium silicate, barium borosilicate, strontium borosilicate, borosilicate, lithium silicate, amorphous silica, calcium phosphate, calcium carbonate, alumina,  
35 aluminium zirconia, tin oxide, tantalum oxide, niobium oxide, and titania glass,



carbon black, graphite, cristobalite, silica, zircon-silica, calcium metasilicate (e.g. wollastonite), calcium magnesium silicate, and mixtures thereof.

4. A method according to any one of the preceding claims; wherein said  
5 filler core material comprises or is in the form of (porous and non porous) particles, preferably having particle diameters in the range from about 0.001  $\mu\text{m}$  (1 nm) to about 4 mm, such as for dental use 0.001-100  $\mu\text{m}$ , such as 1 mm to 4 mm for use in road marking materials, such as from 0.5 to 3000 in paints.
- 10 5. A method according to any one of the preceding claims, wherein said filler core material comprises or is in the form of fibers (chopped and non-chopped, single crystalline and polycrystalline single filaments and polyfilaments), such as fibers with an aspect (length to diameter) ratio of 2 to  
15 1000, such as from 2 to 300, such as from 3 to 200, preferably maintaining an aspect ratio of at least 20, the diameter preferably being in the range of 0.001  $\mu\text{m}$  to 100  $\mu\text{m}$ .
- 20 6. A method according to any one of the preceding claims, wherein said filler core material comprises or is in the form of a woven or non-woven fiber unit, such as a fiber mat.
- 25 7. A method according to any one of the preceding claims, wherein said filler core material is of an inorganic material.
8. A method according to any one of the preceding claims, wherein said  
30 silane coupling agent is a silane or a silanol (hydrolyzed silane), the silane coupling agent preferably being a monomeric, oligomeric and polymeric alkoxy- or chlorosilane coupling agent, preferably a ethylenically-unsaturated alkoxy- or chlorosilane coupling agent, more preferably a silane coupling agent comprising at least one of the groups vinyl groups, allyl groups, alkyl groups, styryl groups, aromatic groups, chloromethylaromatic groups, amino groups, isocyanate groups, halogen atoms such as fluorine or chlorine or bromine atoms, epoxide groups, mercapto groups, acrylic groups, metacrylic groups,  
35 silazane groups, and azido groups.

9. A method according to any one of the preceding claims, wherein said silane coupling agent is selected from the group consisting of the following silanes or the corresponding silanols: vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri-(2-methoxyethoxy)-silane, vinylbenzylcationic silane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane, isocyanatoethyltrimethoxysilane, isocyanatopropyltrimethoxysilane, isocyanatopropyltriethoxysilane, N-(3-trimethoxysilylpropyl)-N-methyl-N,N-diallyl ammonium chloride, trimethoxysilylpropylisothiuronium chloride, N-trimethoxysilylpropyltributyl ammonium bromide, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -chloropropyl trimethoxysilane; n-alkylsilanes, n-alkyldichlorosilanes, n-alkyltrichlorosilanes, such as n-hexyltrichlorosilane, n-octyltrichlorosilane, n-decyltrichlorosilane, n-dodecyltrichlorosilane, and mixtures thereof.
10. A method according to any one of the preceding claims, wherein said silane coupling agent has a molar weight of up to about 500 g/mol, such as between 150 and 400 g/mol.
11. A method according to any one of the preceding claims, wherein said treatment medium containing CO<sub>2</sub>, is in its liquid state during the treatment step, said silane coupling agent preferably being partly or totally dissolved or dispersed in the treatment medium containing CO<sub>2</sub>.
12. A method according to any one of the preceding claims, wherein said CO<sub>2</sub> is in its supercritical state during the treatment step, said silane coupling agent preferably being partly or totally dissolved or dispersed in said CO<sub>2</sub>.
13. A method according to any one of the preceding claims, wherein said CO<sub>2</sub> is changing from its liquid state/gas state to its supercritical state during the treatment step.

14. A method according to any one of the preceding claims, wherein said treatment medium comprises at least 50 % by weight, such as at least 75 % by weight, such as at least 85 % by weight, such as at least 90 % by weight, such as at least 95 % by weight of CO<sub>2</sub>, such as essentially pure CO<sub>2</sub>.

15. A method according to any one of the preceding claims, wherein said treatment medium comprises up to 50 % by weight of water, such as up to 25 % by weight of water, such as up to 10 % by weight of water, such as up to 5 % by weight of water, such as up to 1 % by weight of water.

16. A method according to any one of the preceding claims, wherein said treatment medium comprises up to 50 % by weight of an organic solvent such as alcohols, ketones, paraffins, ethers, amines, aromatics, such as up to 25 % by weight of organic solvent, such as up to 10 % by weight of organic solvent, such as up to 5 % by weight of organic solvent.

17. A method according to any one of the preceding claims, wherein said treatment medium comprises up to about 3 %, such as up to about 1 %, such as up to about 0.2 % by weight of surfactants.

18. A method according to any one of the preceding claims, wherein the amount of silane coupling agent to treatment medium is between 0.001:1 w/w and 1:1, preferably in the range of 0.01:1 w/w and 0.1:1.

19. A method according to any one of the preceding claims, wherein the pH value of the treatment medium is either 5 or less or 8 or higher to thereby promote hydrolysis of the silane.

20. A method according to any one of the preceding claims, wherein said filler core material is subjected to a cleaning step prior to the silane treatment step, said cleaning step preferably comprising the step of subjecting the filler core material to a cleaning medium comprising CO<sub>2</sub>.

21. A method according to claim 20, wherein said cleaning medium and said treatment medium have essentially equal composition.

22. A method according to any one of the preceding claims, wherein said  
5 silane treated filler core material is subjected to an impregnating step comprising depositing additional components to the silane treated filler core material.

23. A method according to claim 22, wherein said impregnating step  
10 comprises depositing one or more impregnating components in the form of organic components, such as polymer or polymer precursors (including monomers, dimers and oligomers) to the silane treated filler core material, said impregnating components preferably being added from an impregnating medium comprising CO<sub>2</sub>.

15 24. A method according to any one of the claims 22-23, wherein said impregnating component(s) is selected from the group consisting of -mono or multifunctional monomers, such as monomers comprising one, two or more ethylenically unsaturated double bonds e.g. including unsaturated amides  
20 such as 2-acrylamidoglycolic acid, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, tetra acrylamido glycuril ("TAGU") and diethylenetriamine tris-acrylamide; -linear, branched or cyclic polymer of ethylenically unsaturated monomers, polyester, polyamide, polyether, polyethyleneglycol, polysaccharide, cellulose, polypropylene,  
25 polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde; and mixtures thereof.

25. A method according to any one of the claims 22-23, wherein said  
30 impregnating component(s) is selected from the group consisting of mono-, di- or polyfunctional acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, styryl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol  
35 dimethacrylate ("TEGDMA"), tetraethyleneglycol dimethacrylate,

polyethyleneglycol dimethacrylate (e.g., "PEG200 DMA", "PEG400 DMA" and "PEG600 DMA" with an average of 4.5, 9 and 13.6 ethyleneglycol groups or "units" respectively), 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,3-butanetriol  
 5 trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, tris-hydroxyethylisocyanurate triacrylate, beta-methacrylaminoethyl methacrylate, 2,2-bis[4-(2-  
 10 hydroxy-3-methacryloyloxy-propoxy)phenyl]propane ("BIS-GMA"), 2,2-bis[4-(2-methacryloyloxyethoxy)-phenyl]propane, 2,2-bis[4-methacryloyloxy-phenyl]propane, "SARTOMER" 350 ("SR350", Sartomer Corp.) and mixtures thereof.

15 26. A method according to any one of the preceding claims, wherein said silane treated filler core material is subjected to a curing step for further curing of the silane coating and optional impregnation of the coating, said curing step preferably including subjecting the silane treated filler core material to increased temperature.

20 27. A method according to any one of the preceding claims, wherein said silane treated filler core material is subjected to a final rinsing step for removing soluble products, said rinsing step preferably including subjecting the silane treated filler core material to a flushing with a flushing medium  
 25 comprising CO<sub>2</sub>, such as at least 50 % by weight, such as up to about 75 % by weight, such as up to about 85 % by weight, such as up to about 90 % by weight, such as up to about 95 % by weight of CO<sub>2</sub>, such as essentially pure CO<sub>2</sub>, the remaining of the flushing medium preferably consisting of water, organic solvents and/or surfactants.

30 28. A method according to any one of the preceding claims, wherein said silane treated filler core material is subjected to a drying step.

35 29. A method of producing a composite material comprising the steps of producing a silanized composite filler using the method as defined in any one

of the claims 1-28, mixing said silanized composite filler with an optionally curable composite matrix material to provide either a composite material with increased filler-matrix adhesion due to increased chemical compatibility or to provide a precursor composite material, and curing said precursor composite material (by temperature or radiation).

30. A method according to claim 29, wherein said composite matrix material is selected from the group consisting of -linear, branched or cyclic polymer of monomers such as ethylenically unsaturated monomers or difunctional materials such as diols, diamines, diisocyanates, dicarboxylic acids, the thus derived polymers being selected from the group of polyester, polyamide, polyether, polyethyleneglycol, polysaccharide, cellulose, polyethylene, polypropylene, polybutylene, polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), polystyrene, polysulfone, polycarbonate, fluoropolymers such as polytetrafluoroethylene, polyvinylidene fluoride, synthetic and natural rubber, thermoplastic elastomer, silicone rubber, phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde, and mixtures thereof.

31. A method according to claim 29, wherein said composite matrix material is selected from the group consisting of mono-, di- or polyfunctional acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, styryl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate ("TEGDMA"), tetraethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate (e.g., "PEG200 DMA", "PEG400 DMA" and "PEG600 DMA" with an average of 4.5, 9 and 13.6 ethyleneglycol groups or "units" respectively), 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,3-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, tris-hydroxyethylisocyanurate triacrylate, beta-methacrylaminoethyl methacrylate, 2,2-bis[4-(2-hydroxy-3-

methacryloyloxy-propoxy)phenyl]propane ("BIS-GMA"), 2,2-bis[4-(2-methacryloyloxyethoxy)-phenyl]propane, 2,2-bis[4-methacryloyloxyphenyl]propane, "SARTOMER" 350 ("SR350", Sartomer Corp.) and mixtures thereof.

5

32. A method according to any one of the claims 29-31, wherein the curing between the silanized filler and the composite matrix is afforded by cross linking saturated or unsaturated organic groups attached to both the filler and present in the composite matrix, said cross linking e.g. being provided by  
10 applying radiation such as UV-light or gamma-radiation and/or by activation (decomposition) of previously admixed peroxides or azocompounds such as dicumylperoxide or bis-[t-butylperoxy] compounds or azo-bis-isobutyronitril.

33. A method according to any one of the claims 29-32, wherein said  
15 composite material is a composite material for use in the industrial, automotive, aviation and aerospace sector, such as parts which can be produced by injection moulding, extrusion, calendaring or moulding.

34. A method according to claim 33, wherein the composite material is a  
20 polymer glass fiber matrix, the glass fiber matrix has a length to diameter aspect ratio of at least 20, and the polymer matrix is a thermoplast or a non-thermoplast (curable polymer), preferably selected from the group consisting of PE, PP, PA, epoxy, PET and mixtures thereof.

25 35. A method according to any one of the claims 33 and 34, wherein the polymer glass fiber matrix silane coupling agent is selected so that the final glass fiber filler comprises between 0.01 % and 1 %, such as between 0.05 % and 0.5 %, such as between 0.08 % and 0.2 % by weight of the silane coupling agent.

30

36. A method according to any one of the claims 33 - 35, wherein the glass fiber is silanized using octyltriethoxysilan as silane coupling agent and thereafter the silanized glass fibers are mixed with PE, the amount of silane preferably being between 0.2 and 1 % by weight.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/DK2004/000475

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 A61K/083 C03C17/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A61K C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) & JP 09 049829 A (AGENCY OF IND SCIENCE &AMP;TECHNOL), 18 February 1997 (1997-02-18) abstract	1-49
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 02, 2 April 2002 (2002-04-02) & JP 2001 303456 A (DU PONT TORAY CO LTD), 31 October 2001 (2001-10-31) abstract	1-49

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

15 September 2004

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 05, 14 September 2000 (2000-09-14) & JP 2000 053871 A (TORAY IND INC), 22 February 2000 (2000-02-22) abstract	1-49
A	US 5 968 652 A (BABU GADDAM N ET AL) 19 October 1999 (1999-10-19) cited in the application claims	1-49

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Information on patent family members

International Application No

PCT/DK2004/000475

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